# THE
# National Academy of Sciences, India

## THIRTY-NINTH ANNUAL SESSION

### ROORKEE, March, 6, 7, and 8, 1970



## SECTION OF BIOLOGICAL SCIENCES

### PRESIDENTIAL ADDRESS

### The Record of Early Life in Rocks

*By*

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I am grateful, to the National Academy of Sciences for inviting me to preside over the Biology Section of the Thirty-ninth Annual Session.

I have accepted this office with some hesitation, because of the fact that I am neither a Botanist nor a Zoologist. I have, however, taken comfort in the fact that such problems as Organic evolution, antiquity of life on the Earth, etc. are of great interest not only to biologists but also to students of geology.

I have chosen for my address the topic : Record of Early Life in Rocks, a subject in which scientists from many fields are currently deeply interested.

### Introduction

Nearly five billion years have elapsed since the origin of the earth. As man looks back into the dim and distant past, in an attempt to decipher the momentous events that have culminated in the evolution of life through the ages, he is faced with two fundamental questions : what were the steps that led to the development of life and when did life originate on the earth ? Naturally, as in any historical account, it is difficult to piece together evidence of an event that happened in the remote past, but geologists and palaeontologists in many countries including India are attacking the problem of finding records of life in Precambrian era stretching over seven-eighths of the earth's history previously thought to be a biological desert.

Any study dealing with the problem of the record of early life, necessarily encompasses a number of subsidiary problems, which are common to the scientist and the philosopher. How did life originate on this planet ? Could life have developed from inorganic substances ? What were the primitive forms related to ? What influence did the primitive atmosphere have on the origin of life ? How accurately can absolute dates be determined for the evolutionary stages of these primitive forms ? What is the state of preservation of these forms in ancient rocks in various parts of the world ? What are the finds of primitive life in India ? An attempt will be made to discuss some of these points with a view to emphasize the important steps in the growth and development of early life and the record of these organisms in rocks of India.

### Primitive atmosphere

It has been stated by several authors, that the atmosphere present on the earth today, has undergone considerable evolution and modification from its original state at the time of the earth's origin. Many attempts have been made

to determine the constituents of the primitive atmosphere. Important contributions have been made by Abelson (1966) and more recently by Cloud (1968). In the very beginning according to Cloud's simplified model of the early earth, there was no magnetic field, no atmosphere and solar winds swept the earth's surface. Then gradually, gravitational heating, core formation and the formation of a magnetic field took place. Still later, the atmosphere and a hydrosphere developed. The primitive atmosphere consisted $CO_2$, $CO$, $H_2O$, $N_2$ and $H_2$. Free oxygen has been increasing in the atmosphere at a very slow rate. 600 million years ago, it was only 1%. It took another 200 million years to reach the 10% level. It was then that land plants appeared, followed by animals. The present day 20% of oxygen allows the higher forms of life to live and function.

### Evolution of organic complexes

It is now a fairly well established fact that the living organic molecules complexes could have originated from inorganic substance. Many theories pertaining to such an origin have been suggested notably by Oparin (1953), Haldane (1954), and still more recently by a number of other biochemists. Strecker (1845) was the first to report synthesis of an amino acid by treating acetaldehyde ammonia with HCN and HCl. Since then, great strides have been made in the biochemical synthesis of various organic complexes including the synthesis of nucleic acids. These studies show, that a variety of organic complexes with characteristics of living organisms, could have been formed on the primitive earth.

Haldane (1929) was one of the first to point out that ultra violet radiation in a primitive atmosphere in the absence of $O_2$ could produce 'A vast variety of organic substances' from what he termed a 'hot dilute soup'. Recent experimental investigations have resulted in a great deal of data about the fundamental nucleic acids, namely DNA and RNA, which control the life processes of organisms. It is hoped the present decade will answer a number of questions on the synthesis of these acids and the problems of heredity assimilation and reproduction.

### Amino-acids in Precambrian rocks

Support for the synthesis of organic acids by primitive organisms comes from the discovery of amino-acids from rocks containing the earth's earliest fossil forms. Schopf, Kvenvalden and Barghoorn (1968) among others, have reported aminoacids, hydrocarbons, porphyrins and fatty acids from rocks as old as 3·1 billion years in the Fig Tree chert of South Africa, also from the 1·9 billion years old Guaflint cherts on the northern shores of Lake Superior and, lastly from the Bitter Springs formation of central Australia, which is 1 billion years old. We owe to Ramsay (1963) an eminent structural geologist from London for the first information about the record of ancient life in the Fig Tree Series.

### Oldest and most primitive fossils

From the biological view point, one would expect primitive organisms to be unicellular (in form) and microscopic in size. It is, therefore, not surprising that the oldest fossils discovered to date in black, carbon-rich sedimentary rocks of South Africa, 3·1 billion years are of this type. Barghoorn and Schopf (1965) reported such microscopic, bacterium-like organisms $0.5\mu$ in length and $0.25\mu$ in cross section, which they studied with the help of electron microscope. They also discovered that the fossils, which they called *Eobacterium isolatum*, were similar to

the present day rod-shaped bacteria and possessed a two layered cell wall. Recent analyses also indicate the presence of other lowly organisms, such as algae, capable of photosynthesis. Plumstead (1969) has thrown considerable light on these primitive forms.

*Middle Precambrian Micro-organisms*

The next record of primitive life comes from the pioneering research by Tyler and Barghoorn (1954) in the black cherts of Gunflint Iron formations exposed in the Lake Superior region of Canada and North America. The organisms which occur abundantly and are quite diversified, have been dated at about 2 billion years. The most prominent fossil forms, are unbranched filaments and reticulate spherical bodies. These fossils share a remarkable similarity with the interlacing algal filaments, so common in modern communities of aquatic algae. A significant step in the evolution of these primitive forms seems to be the dominance of photosynthetic forms.

Of special interest to the biologist is the Middle precambrian Gunflint genus *Kakabekia umbellata*. This organism which consists of a basal ellipsoidal bulb attached to a membranous umbrella like crown by a tubular thread like stipe, is the most distinctive and abundant organism in the cherts. Recent work, has shown that this primitive Precambrian form is apparently generically indistinguishable from a present day non-photosynthetic organism found in a soil sample in Wales by two workers Siegel and Giumarro.

*Late Precambrian Life*

Late Precambrian forms show a higher evolutionary grade of development than those recorded from older rocks. Also, much evidence has been collected from various continents to indicate that life was not only widespread during this period but that it was also quite prolific. Primitive green algae, aquatic fungi and probable protozoan animals are some of the organisms reported from late Precambrian rocks with an antiquity of a billion years.

The 1·1 billion years belt series of South central Montana is remarkable for the presence of blue green algae, fungi, spores and microscopic, and multichambered tests, which represent the probable ancestors of Foraminifera. Further east, the Nonesuch shale of North Michigan contains the best documented evidence of biological activity yet discovered in Precambrian sediments. The presence of pristanes, phytane, and carbon isotopes indicates the existence of photosynthetic organisms, also vanadium–porphyrin complexes, derived from the chlorophyll molecule are the oldest reported occurrence of definite chlorophyll matter. Optically active organic compounds, known only to be synthesized by organisms are present in the crude oil occurring in the Nonesuch shale. The process of photosynthesis has in progress for some 2,000 million years, a source for continuous propagation and accumulation of free oxygen, and as we know photosynthesis is the ultimate energy source of all biological activity.

The Bitter Springs formation of central Australia contains the best preserved of all Precambrian fossils yet described. This Australian microflora consists of filamentous blue green algae, spheroidal green algae and rod-shaped and coccoid bacteria. Recently Misra, S. (1969), my former student, has described four catagories of organic impressions from the late Precambrian of southeastern New Foundland.

### The Earliest Record of Life in India

Although rocks, comparable in age to the 3 billion years old Fig Tree forma-tion of South Africa, are present in India, they have as yet yielded no fossils. The oldest forms of life to be recorded from India are from the Dharwar sediments ranging back into time to 2 billion years. Gowda and Sreenivasa (1969) have reported circular, elliptical, triangular and oval bodies called acritarchs from the Guddadaranga-yanhalli formation. The next record of Precambrian life comes from the slightly younger Aravalli strata of Rajasthan. Muktinath and Sant (1967) have reported algal stromatolites associated with phosphorite deposits near Udaipur.

### Cuddapahan Life

The next younger in sequence of rocks known as the Cuddapah System extending northwards in an area from Madras to Bazwada has yielded organic remains. Radioactive analysis of galena veins by Aswathanarayana (1962) has revealed an age of 1·450 million years. Still more recently, the Russian geolo-gists Vinogradov, Tugarinov and others have reported ages as high as 1,600 million years but no lower than 1,160 million years. This greater age was quite unexpect-ed for the Cuddapahas as these beds were believed to be younger. The fossil finds, in these formations become consequently all the more significant. The Cuddapahs are lithologically ideal for preservation, but fossils are restricted to certain horizons in the lower Cuddapahas.

The most common type of fossils to be described from the area, are algal stromatolites. Their algal affinities were first noticed by Srinivasa Rao (1944). These colonies of calcareous algae called *Collenia* are available in size, generally showing a rounded, elevated surface. The rounded surface are separated usually by massive limestone, but in a few exceptional cases may consist of numerous rounded or ovoidal patches separated by a reddish brown, highly calcareous mud. A detailed investigation of such bodies reveals a crowded colony of developing algae. Individuals are about 2·5″ in length and an inch in diameter. They are conical in shape and wider distally. The individuals appear to be separated at the top, but united at the base. Other varieties of algae described by Srinivasa Rao (1949) include annular, filamentous, tabular and branched forms. Vishwa-nathiah, Rajalu and Sathyanarayana (1964) have also reported stromatolitic lime-stones in the Lower Kaladgis near Mysore. Sahni and Shrivastava (1962) reported from Cuddapah equivalents a series of spores, which by all accounts belong to perhaps highly developed plant forms.

### Vindhyan Life

The next younger record of life comes from a series of rocks known collec-tively as the Vindhyan System exposed in a wide belt covering some 104,000 square kilometres in Central India. A number of fossil forms have been reported from Vindhyan sediments (Misra and Awasthi, 1962) and evidence concering life during this period is increasing day by day. Geochronologic methods have indicated an age of 1,110 million years for rocks exposed near Ghurma in Mirzapur district (Vinogradov and Tugarinov, 1964). Though an accurate age estimation of the Vindhyan sediments is at present a matter of some contro-versy, evidence from current researches indicates a Precambrian age for the major part of the Vindhyan formations.

For the past two decades, I have been engaged in the study of the record of life from Vindhyan rocks. A number of diverse and varied forms of life from

indirect and direct evidences have been reported by many workers. These include carbonaceous matter, organic markings, plant remains and even some animal remains, although doubtful. In order to deal with the fossil forms more effectively. I shall divide the finds into two broad categories : (a) tracks, trails, worm burrows and other doubtful fossils, and (b) plant remains.

As the first subdivision affords only indirect and ambiguous evidence of life during Vindhyan times, we shall confine ourselves to the second subdivision, namely plant fossils in these sediments.

Vindhyan fossils consisting of small, carbonised discs (*Fermoria*) were first reported as early as 1907–1908 by Jones from the Suket shales near Rampura in Madhya Pradesh. The nature of these fossils was to become later a matter of controversy. Though originally described as invertebrate Brachiopods by Jones and Chapman, their plant affinities were pointed out by Howell and their algal nature by Sahni and Shrivastava (1954). Qualitative chemical analysis led me to believe (Misra, 1951 ; Misra and Dubey, 1952 ; Misra, 1957) that the discs may have had an inorganic origin. Recently, Maithy (1968) has described acritarchs from the Suket Shales of the Kaimur series. One of these forms superficially resembling the genus *Fermoria* has been identified as *Tasmanites*.

Other plant microfossils have been reported by Ghosh and Bose (1950) and Bose, (1956). These forms include monosaccate and disaccate spores. Sitholey, Srivastava and Verma (1953) have described types belonging to cyanophyceae, unicellular algae, fungal spores, filamentous bodies, circular discs and desmids.

Apart from the above mentioned remains, algal stromatolites have been reported from a wide area from Vindhyan strata (Mathur, Narain and Srivastava, 1958) and other younger Precambrian formations in the Himalayan region. Stromatolites have been described from the Calc Zone of Pithoragarh (Misra and Valdiya, 1961) from the Lower Shali Limestone of Tatapani, near Simla (Valdiya, 1962), and more recently from a number of carbonate formations of the lesser Himalayas (Valdiya, 1969). In a detailed and comprehensive work, my former student and colleague Valdiya (1969) has shown the affinities of the algal stromatolite *Collenia baicalica* from Precambrian sediments in Pithoragarh, Dehra Dun, Mahasu and Ambala districts to forms typical of the stromatolite complex of U. S. S. R., approximately 1,200 to 1,000 million years in age.

## Summary and Conclusion

In the course of this discussion, we have attempted to give a panoramic view of the origin of life through the developing stages of the earliest organisms. There was a gradual increase in the complexity and abundance of forms from rocks 3 billion years old to rocks, ½ billion years (in age). Present evidence, indicates that algae predominated over other forms of life not only in their diversity and abundance but also in their cosmopolitan distribution.

The study of ancient sediments of organic origin is also of considerable interest in the search for minerals. It appears that metalliferous deposits of iron, copper, lead, zinc, vanadium and uranium in sedimentary rocks can also have organogenetic origin. One might cite the example of association of carbon with gold and uranium in the 2,200 million years old Witwatersrand deposits. The gold content increases with the increase of carbon percentage.

Much research remains to be done in the field of primitive organisms and this branch of science is one in which the biologist and geologists must work side by side to piece together data concerning, early life.

# References

Abeison, P. H.   Chemical events on the Primitive earth. *Proc. Nat. Acad. Sci. U.S.A.* **55** : 1365–72, 1966.

Aswathanarayana, H.   Age of the Cuddapahs, India. *Nature,* **194** : 4828, 1962.

Barghoorn, E. S. and Schopf, J. W.   Micro-organisms from the Late Precambrian of Central Australia. *Science,* **150** : 337–39, 1965.

Bose, A.   Plant life in Vindhyans. *Nature, Lond.,* **178** : 927–928, 1956.

Chapman, Frederick.   Primitive fossils, Possibly a tramatous and Neotramatous Brachiopoda from the Vindhyans of India. *Rec. Geol. Surv. India,* **69** : 109–20, 1936.

Cloud, E. Preston, Jr.   Premetazoan Evolution and the Origins of the Metazoa. *Symposium 100th Annivers. P.M.N.H. at Yale Univ.,* 1968.

Ghosh, A. K. and Bose, A.   Microfossils from the Vindhyans. *Sci. and Cult.* **15** : 300–331, 1950.

Gowda, S. Sambe and Sreenivasa, T. N.   Microfossils from the Archaen Complex of Mysore. *Journ. Geol. Soc. Ind.,* **10**(2) : 201–208, 1969.

Haldane, J. B. S.   The Origin of Life, *New Biol.,* **16** : 12–27, 1954.

Howell, B. F.   Evidence from Fossils of the Age of the Vindhyan System. *Journ. Palaeont. Soc. Ind.,* **1**(1) : 108–112, 1956.

Jones, H. C.   In General Report; *Rec. Geol. Surv. India,* **38** : 66, 1909.

Maithy, P. K.   On the Occurrence of Microremains from the Vindhyan Formations of India. *The Palaeobotan.,* **17**(1) : 48–51, 1968.

Mathur, S. M., Narain, K. and Srivastava, J. P.   Algal Structures from the Fawn Limestone, Semri Series (Lower Vindhyan) in the Mirzapur District. *Rec. Geol. Surv. Ind.,* **87** : 819–822, 1958.

Mathur, S. M.   Indophyton. A New Stromatolite from genus. *Current Science,* **34** : 84–85, 1965.

Misra, R. C.   A new collection of Fossils from the Suket Shales (Vindhyans). *Curr. Sci.,* **20** : 23, 1951.

Misra, R. C. and Dube, S. N.   A new collection and restudy of organic remains from Suket Shales (Vindhyans), Rampura, Madhya Pradesh. *Sci. and Cult.,* **18** : 46–48, 1952.

Misra, R. C.   Fermoria, the enigma of Indian Palaeontology. *Journ. Palaeont. Soc. Ind.,* **2** : 54–57, 1957.

Misra, R. C. and Valdiya, K. S.   The Calc Zone of Pithoragarh, with special reference to occurrence of stromatolites. *Journ. Geol. Soc. Ind.,* **2** : 78–96, 1961.

Misra, R. C. and Awasthi, N.   Sedimentary Markings and Other Structures in the Rocks of the Vindhyan Formations of the Son Valley and Maihar-Rewa Area, India. *Journ. Sed. Petrol.,* **32** : 764–775, 1962*b*.

———   Fossil finds from the Vindhyan Formations of India. *Bull. I.S.M. Geol. Soc. S. K. Roy Comm., Vol.* 102–109, 1962*a*.

Misra, R. C.   The Vindhyan System. *Presidential Address, Ind. Sci. Congr. 59th Session, Bombay (Powai),* 1–32, 1969.

Misra, S. B.   Late Precambrian (?) Fossils from Southeastern New Foundland. *Geol. Soc. America Bulletin,* **80** : 2133–2140, 1969.

Oparin, A. I.   The origin of Life.   2nd ed. of a translation by S. Morgulis from the 1936. *Russian edition, Dover. New York,* 270, 1953.

Plumstead, E. P.   Reflections on the Earliest plant life and its great contribution to the life of today. *J. Sen Memorial Vol. Bot. Soc. Bengal,* 339–348, 1969.

Ramsay, J. G.  Structural Investigations in the Barberton Mountain Land, Eastern Transvaal, University Witswatersrand. *Econ. Geol. Res. Unit Information Circular,* **14** : 1–44, 1963.

Rao, M. R. S.  Algal Limestones from the Pre-Cambrians of South India. II *Curr. Sci.,* **13** : 75, 1944.

Sahni, M. R. and Shrivastava, R. N.  New Organic Remains from the Vindhyan System and the Probable Systematic Position of *Fermoria* Chapman *Curr. Sci.,* **23** : 39–41, 1954.

Schopf, Wolloam, J., Kvenvolden, Keith, A. and Barghoorn, S. E. Amino-. acids in Pre-Cambrian Sediments. *Proc. Nat. Acad. Sci.,* **59**(2) : 639–646, 1968.

Sitholey, R. V., Srivastava, P. N. and Verma, C. P.  Microfossils from the Upper Vindhyans with a discussion on the age of the Vindhyans in the light of plant fossil discoveries. *Proc. Natn. Inst. Sci. India,* **19**(2) : 195–202, 1953.

Srinivasa Rao, M. R.  Algal Structures from the Cuddapah Limestone (Precambrian), South India. *Journ. Mysore University,* **9** : 67–72, 1949.

Tyler, S. A. and Barghoorn, E. S.  Occurrence of Structurally preserved plants in the Pre-Cambrian Rocks of the Canadian Shield.  *Science,* **119** : 106-08, 1954.

Valdiya, K. S.  Note on the Discovery of Stromatolitic Structure from the Lower Shali Limestone of Tatapani, near Simla, H. P.  *Current Science,* **31** : 64-65, 1962.

Valdiya, K. S.  Stromatolites of the Lesser Himalayan Carbonate Formations and Vindhyans. *Journ. Geol. Soc. Ind.* **10**(1) : 1969.

Vinogradov, A. and Tugarinov, A.  Geochronology of Indian Precambrian. *22nd Intern. Geol. Congr. Late Abstract,* 1964.

Vishwanathiah, M. N., Rajulu, B. V. G. and Sathyanarayan, S.  Stramatolitic Limestone in the Lower Kaladgis (Precambrian), Mysore State. *Bull. Geol. Soc. Ind.,* **1** : 25-27, 1964.

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## SECTION OF PHYSICAL SCIENCES

### PRESIDENTIAL ADDRESS

## Parachor of Ions, Resonance and Hydrogen Bonding

*By*

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# PRESIDENTIAL ADDRESS

## Parachor of Ions, Resonance and Hydrogen Bonding

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MEMBERS OF THE ACADEMY, LADIES AND GENTLEMEN

I am extremely thankful to the Council of the National Academy of Sciences for electing me as the President of its Physical Sciences Section this year. I still remember the day in 1930 when as a student I read my paper on 'Relation between Intensity and Velocity of Photo chemical Reactions', before the first meeting of this Academy, held in Physics Lecture Theatre of Allahabad University with Dr. Meghnath Saha in Chair. When I finished deriving my expression, Dr. Saha remarked, 'It could be done in few steps.' 'Come to the Board' was my reply. It was quite natural that I was immediately snubbed by my Guru, Dr. Nil Ratan Dhar, for my rudeness. It was never expected that this very rude student would be called upon after forty years to deliver the Presidential Address of the Physical Science Section of the same Academy. I am fully aware of my inability and incapability in fulfilling the task to which I am put, but I am confident that when the Council took the decision for a person like me, the Academy must have decided to offer me full co-operation and see that I am successful. Further, there are here distinguished persons like my own Guru who will see that I do not fail in my task.

Let me take this opportunity of congratulating the authorities of Roorkee University especially the Vice-Chancellor for willingness with which they have come forward to have 39th Annual Session of the National Academy of Sciences here. Only with such help and encouragement Scientific research can advance in any country. I am sure that this encouragement will continue for ever.

The Science has developed within last thirty years with such a rapid rate, that it is impossible to keep pace with it. This is particularly so, for us old scientists. It is my firm opinion that our younger generation is doing far better than what we did at their age in our own times.

In my address, I have decided to discuss before you the work on 'Parachor' concerning ions, resonance and hydrogen bonding.

*Parachor of Ions.*

Sugden[1] suggested that polar bond should have the same parachor of $-1\cdot6$ units, as the semipolar double bond, since this bond is made up of a covalent bond (whose contribution is zero) and of an electrovalent bond. It was surprising that he should have come to this conclusion inspite of his own data[2] where the fall in parachor due to electrovalent bond was found to occur in some cases to the extent of $54\cdot5$ units. Again in calculating the atomic parachors of alkali metals from the parachors of their fused salts from the results of Jaeger[3], Sugden and

Wilkins[2] have employed the same values of parachor for ions and atoms, making an allowance of -1·6 units for electrovalent bond. This cannot be reconciled with the theory of Born[4] which implies that positive ions occupy smaller and negative ion a larger volume, than the corresponding atom in combination.

Mumford and Phillips[5] were the first to distinguish between atomic and ionic parachors but did not show that ionic parachor was an additive property. On the assumption that radius of similarly constituted atoms and ions is determined by the distribution of the outermost electrons and is inversely proportional to the effective nuclear charges, they showed on the basis of wave mechanics[6], that the parachor values of halide ions should on an average be 1·46 times those of the atoms of the corresponding rare gases and thus about 1·44 times those of the halogen atoms in non-polar combination.

Lakhani and Daroga[7] and Ray[8] simultaneously studied the parachor of salts in aqueous solutions by using Hamick and Andrews[9] equation as applied to mixtures. The former author's have used the expression $P_m = (1 - x) P_p + x P_x/2$, instead of the usual one $P_m = (1 - x) P_p + x P_x$, on erroneous assumption, that when a solid is dissolved, the values of parachor would become half. We[10] have shown theoretically that the usual equation remains unaffected whether a solid or liquid is dissolved. This was further confirmed[11] by determining the Parachor of the same substance in fused and in dissolved state.

Ray[8] has clearly indicated that ions should have separate parachor values and yet, he employed atomic values in his consideration. He observed that parachors of electrolytes are far lower than those calculated on atomic basis. He further stated that Mumford and Phillips[5] values for ions do not reproduce the observed results. However, he has confused his discussion by introducing the concept of degree of ionisation in case of parachors of strong electrolytes which are known to be completely ionised.

It was shown by us[12] that Kolhrausch law, applicable to mobilities of ions, holds in case of parachor. or $P_{NaCl} - P_{KCl} = P_{NaBr} - P_{KBr} = P_{NaI} - P_{KI}$.
This was done from our own results as well as from Jaegers[3] results on fused salts. Our value was about 29, while that from Jaegers'[3] it was 31. It was thus established that ionic parachor is an additive property and hence specific values could be attributed to ions.

The main problem now was how to get the parachor of one ion independently, so that the values for other ions could be fixed. The idea of connecting the properties of compounds with their electronic configuration originated with Langmuir[13] who applied it to isomorphism. On this basis $O_2^{-2}$, $F^-$, Ne, $Na^+$, $Mg^{2+}$ are isosters and assumed to have similar properties. Thus, isomorphism of NaF and MgO was attributed to the similarity of their property, namely, to the orientation of the oppositely charged ions in the crystals of their compounds. Copley[14] introduced this idea of isoelectric isosters to parachor. We[12] extended the suggestion and it was concluded that the anions $O^{-2}$ and $F^-$ as well as the cations $Na^+$ and $Mg^{2+}$ should have the same parachor as Neon. On this basis the Parachor of KCl should be twice that of Argon, the parachor of NaCl should be equal to the sum of the parachors of Neon and Argon and the parachor of NaF should be twice of Argon. The values for Neon and Argon are 25 and 54 respectively[15]. The calculated and observed values are :

|            | NaCl | KCl   | NaF  |
|------------|------|-------|------|
| Calculated | 79   | 108   | 50   |
| Observed   | 79·6 | 108·9 | 50·2 |

It may be stated that the value of KCl observed previously by Ray[8] was also of the same order. These values are far smaller than those calculated from fused salts. Clearly there is a difference, since above results are in solution, and there can be no comparision between the values calculated in fused state and in solution.

Kaweeshwar and Vaidya[16] have criticised the above work on the ground that isosterism and isomorphism do not always go together. Further, isosteric ions may not have the same size. Basing their ideas on the views of Jones and Ray[17], Silverman[18] and Lee[19], they have associated parachor with ionic radius. Further, taking advantage of our[11] observation that parachor of fused salt is practically the same as in dissolved state, they have calculated ionic parachors with the help of Triche's[20] work on ionic parachor for dissolved state, from the fused salt values obtained from Jaegers[3] work. It is natural for these values to reproduce the parachor of fused salt as they are derived from them, but they fail to reproduce experimental values in solution. In both Mumford and Phillips work[5] as well as of Kaweeshwar and Vaidya[16] one value alone is determined independently, while other is obtained merely by substraction from the experimental value of the salt. In our case both the values are determined independently of the parachor value of the salt in aqueous solutions and therefore stands on sounder basis. Recently, Liska[21] has evaluated parachor values of a number of inorganic salts in water and come to the conclusion that additive law is not applicable to aqueous solutions of inorganic salts due to deforming action of oppositely charged ions. On the whole, it may be said that though it is established that ions should lower, the parachor values considerably the exact values for ions is a problem which still needs further investigation. It will be shown that lowering of parachor due to electrovalent bond has very great significance in deciding the nature of hydrogen bond.

*Parachor and Resonance*

It is well known that there are many substances whose properties cannot be accounted by means of a single electronic structure of valence-bond type. Pauling[22] has introduced the idea of 'resonance' amongst two or more such structures. According to wave mechanical theory of resonance the actual molecule can be written at least approximately, as the linear combination of the orbital functions of separate structures. One of the solution of the approximate equations should give a value which is less than that of any of the individual structures. It is obvious that various resonance structures should not differ much from one another in their potential energy.

There are various methods for detecting the existence of resonance such as resonance energy,[23] heat of formation[24], and measurement of internuclear distances[25] in the compound. Dipole moment[26] has also been successfully used to establish the existence of resonance. We[27] have made an attempt to relate resonance to parachor.

Since the resonance structures should have potential energies very near to each other, it is suggested that those structures will only be possible whose parachors are the same or nearly the same. However, there will be slight lowering in the parachor due to polar nature of the some of the resonance structures. This lowering should be 1·6 units the value for semipolar bond suggested by Sugden but may be larger if there are number of polar resonance structures. Further, the constancy of the value −1·6 has been questioned on the ground that the extent of polarity varies with the nature of the combining atoms. Also, when there is complete ionisation, as in case of strong electrolytes in aqueous solutions, the value has been
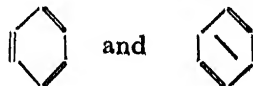
[ 3 ]

shown to fall[8,12] by several units. It is thus possible to decide from the comparison of the observed and the calculated parachors of the various possible structures whether resonance exists amongst them.

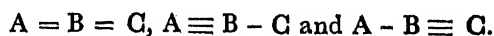The common resonance structures are :

(i) Those in which bonds exchange positions.

$$A = B - C \text{ and } A - B = C$$
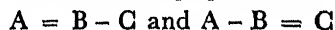
(ii) Those in which a double bond changes to two rings of four

 and 

(iii) Those in which two double bonds are replaced by a triple bond and a single bond

$$A = B = C, \; A \equiv B - C \text{ and } A - B \equiv C.$$

Obviously there are some other types but the above ones are the main.

If our suggestion that parachors of resonance structures be not very different from one another is correct, then in all the three cases mentioned above the various forms of resonance structures should have the same or nearly the same parachor.

In case (i) there is no difficulty as the number and the type of bonds remain the same. The typical examples are alkyl nitro compounds and alkyl amides.

 and 

 and 
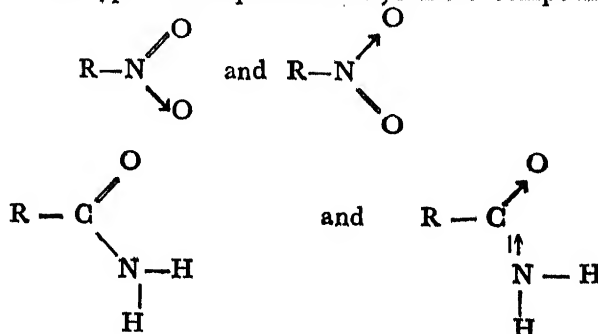
The observed parachor for nitro group is 73·1 while the calculated value for each structure is 74·1. The slight lowering is due to polar nature of the structure as stated. There is a third possible structure.
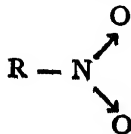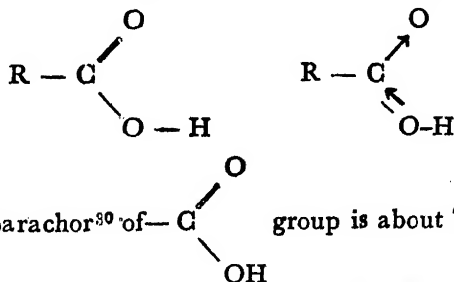


The calculated parachor for this structure will be less by 23·1 units as one double bond has disappeared and will be very different from observed value. According to parachor theory of resonance therefore, this structure is not possible. Pauling[28] also states that this structure should hardly contribute towards resonance.

[ 4 ]

The observed parachor of acetamide[29] is 148 while the calculated value is 151. This supports our resonance theory, the slight lowering being due to polar nature of the structures.

It has been shown by taking several cases[27] that where the resonance structures have no polar nature, the observed values show only a very slight decrease compared to calculated values. This decrease is larger, greater the number of polar structures contributing towards resonance.

Cases are known where resonance alone is not able to explain the observed lower value of parachor than the calculated one. The well known cases being those of carboxylic acids which have the resonance structures

$$R - C \overset{O}{\underset{O - H}{\big\langle}} \qquad\qquad R - C \overset{O}{\underset{O-H}{\big\langle}}$$

The observed parachor[30] of $-C\overset{O}{\underset{OH}{\big\langle}}$ group is about 75, while the calculated value is about 85. These acids are known to form dimers and will be considered under hydrogen bonding.

In case (ii) of the resonance structures, it will be seen that if parachor values are not to change to satisfy the condition of resonance, it is necessary that the parachor of two rings of four should be equal to the parachor of a double bond, since one double bond disappears from Kekule's structure and two rings of four appear instead, in Dewar's structure. Similarly in case (iii) the parachor of a triple bond should be twice that of a double bond, as in these structures two double bonds disappear and a triple bond and a single bond appear. The interesting confirmation of these conclusions is seen when the values of parachor as given by Sugden[31] are compared.

| Triple bond | 46·6 | A ring of four 11·6 |
|---|---|---|
| Double bond | 23·1 | |

W. Hückel[32] remarked "in case of increments it is striking that for triple bond is exactly twice that of double bond. Whether any theoretical significance can be attached to these relationships between numerical values is a problem". However, he failed to see that the parachor of a double bond is twice that of a ring of four. These relationships, as shown above, are not accidental but arise out of resonance, a fact which was not realised before.

It is well known that the properties of benzene cannot be explained on the basis of a single Kekule's structure. According to parachor consideration the second Kekule's structure is possible, since there is merely an exchange of bonds which does not result in a change in parachor. However, parachor predicts the contribution by Dewar's structure also, though to a lesser extent. In this case, double bond changes to two rings of four resulting in no change in parachor, but the structure being planner, an additional ring of six cannot be assumed. This results in a drop in parachor by 6·1 units as compared to Kekule's structure. This difference is appreciable, hence the extent of resonance between Kekule's and Dewar's structures can only be slight. The calculated values of parachor

for these structures are 207·1 and 201 while the observed value[20] is 206. Thus the main resonance structures are those due to Kekule

However, above considerations clearly show why on parachor basis the resonating structures of Kekule type be always associated with Dewars type though to a very small extent. Claus Armstrong-Bayers centric structures are ruled out as the parachor value is widely different from the observed one. It may be stated that the possibility of a particular resonance structure can only be predicted by comparing the observed and calculated parachor values of various resonance structures suggested.

Incidently, it may be pointed out that we have throughout used Sugden's[31] values for atomic and structural parachors. This point has been critically discussed by us[33]. We have examined the work of Mumford and Phillips[5,34]; Hunter and Maass[30], Edgar and Calingaert[35], Richards, Speyers and Carver[36], Vogel[27], Gibling[28], Quayle and Donaldson[39], Harkins, Clarks and Roberts[40]. There is a fundamental difference in their approach. Sugden desired to see how far the property of parachor can be used for elucidating doubtful structures of molecules, while others have tried to find how far the atomic and structural values when substituted can reproduce the experimental results. The general basis of the property of parachor is thus lost. One example here is enough to support the statement. The value of parachor found for benzene ring, by Vogel[27] is, 1·4, by Gibling[28] 0·0 and 0·8 by Mumford and Phillips[5]. In many aliphatic compounds the value of parachor is above 200, so that an error up to 1·4 units is always possible. The whole distinction between aliphatic and aromatic compounds is lost. The values of Sugden therefore be retained without further criticism.

As stated previously, the parachor of a triple bond is twice that of a double bond and hence the resonance between the structures of the type $A \equiv B - C$, $A - B \equiv C$ and $A = B = C$ is possible. Thus carbon dioxide has the resonance structures, $O = C = O$, $C \rightleftharpoons C \rightarrow O$ and $C \leftarrow C \rightleftharpoons O$. Pauling[41] suggested two more structures, $O = C \rightarrow O$ and $O \leftarrow C = O$. It is interesting to note that observed parachor[42] for $CO_2$ is 77·5 while the value calculated for the first three structures is 91 and 68 for the remaining two. Parachor observations therefore support Pauling's[41] view, that the other two structures also contribute to resonance.

In case of carbon disulphide similar five structures are possible. $S = C = S$, $S \rightleftharpoons C \rightarrow S$, $S \leftarrow C \rightleftharpoons S$, $S = C \rightarrow S$ and $S \leftarrow C = S$. However, the parachor observed[43] is 145 which corresponds to first three structures. The other two structures have parachor value 124 and hence their contribution is nil. This is supported from the study of bond distance of $CS_2$ which comes to be 1·54 Å. Resonance energy[44] of carbon disulphide also confirms the above conclusion.

Parachor theory of resonance has also been successfully employed in explaining the resonating structures of such compounds as carbon oxysulphide[27] SCO, carbon suboxide[27] $C_3O_2$, nitrous oxide[27], hydrazoic acid[27], azido grouping[27] and diazocompounds[27], where two double bonds change to a triple bond and a single bond.

In addition to above cases of normal resonance structures there are typical cases of carbon monoxide and nitroso group. The observed parachor values for them can be used to decide between possible resonance structures. Pauling's[45]

suggestion that $CO$, has the resonating structure $C^+=O^-$, and $C^-=O^+$ is not supported by parachor. The observed value $69\cdot6$ corresponds to the triple bond structure, $C\equiv O$. Pauling's[46] view is supported by the work on dipole moment but not by bond distance.

It will be clear therefore that like resonance energy, bond distance measurement, heat of formation, and dipole moment, parachor can be used to decide between various possible resonance structures. Further, it can suggest as to what resonance structures possible, in a particular case.

*Parachor and Hydrogen Bonding*

Scientists[47] long ago recognised that special theories were necessary to explain the behaviour of associated compounds. Empirically they established that association occurred in those compounds which contained certain functional groups. Alcohols and phenols formed associated complexes whereas hydrocarbons did not. Molecules with hydrogen containing functional groups were recognised to have a particularly tenacious interaction. In 1903, A. Werner[48] proposed that ammonium salt has a configuration in which a proton lies between the ammonia molecule and the ion linking the two. He symbolised the interaction as $(H_3N \ldots H) X$.

Moor and Winmill[49] studied the dissociation constant of various ammonium bases and noted a marked difference between quarternary bases and others. They tried to explain the behaviour on the lines of Werner[48] but failed to appreciate the difference between a proton lying between the molecule and ion and $CH_3$ group lying between the molecule and ion. $\{ N (CH_3)_3 \ldots CH_3 \} OH$. It was Latimer and Rodebush[50] who clearly stated that hydrogen nucleus held between two octets constitutes a weak 'bond'. They arrived at this conclusion from the study of associated liquids. In quarternary bases there is no hydrogen nucleus to form a weak bond with OH and hence it can ionise to act as a stronger base. However, they had no idea as regards the nature of this bond now known as Hydrogen Bond. They did not say whether it was co-valent or electrovalent. The whole idea was centered towards co-ordination due to Werner's[48] suggestion.

Lowery[51] in discussing the polarity of double bonds, assignes co-ordinated position to mobile hydrogen in glutaconic acid but does not seem to have a clear idea since in ethylidene-maleic ester he gives a co-ordination number of four to hydrogen. However, later with H. Burgess[52] he had clearly established the idea of co-ordinated hydrogen from the study of $x$-ray analysis of ice, by the existence of complex ion $HF_2^-$ and from the anamolous properties of oxyacids.

Sidgwick[53] studied the solubilities in water, and boiling points of a series of $o$, $m$, and p–substituted phenols. It was found that with compounds containing certain active groups like $- NO_2$, $- CHO$ and $- Cl$, the ortho derivatives were more volatile, less soluble in water and more soluble in benzene than would have been expected. He therefore concluded that hydrogen atom under certain conditions could increase its co-valency by one.

The above discussion will make it clear that none of these workers had a clear idea of the nature of hydrogen bond. Their ideas were centred with Werner's[48] view of co-ordination. No evidence was put forth that the bond was of co-ordinated type.

Pauling[54] with the help of quantum mechanical theory of valency showed for the first time that a hydrogen atom with only one stable orbital cannot form more than one pure covalent bond and the attraction of two atoms observed in

[ 7 ]

hydrogen bond formation must be due to ionic forces. Since now the hydrogen bond is a bond by hydrogen between two atoms, the co-ordination number does not exceed two. Further, the strength of the bond is not constant but depends on the electronegativity of atoms attached to it, the strength increasing with the increase in the electronegativity of two bonded atoms.

Several classical[55] methods like the determination, of solubility vapour pressure, vapour density, molecular weight, dielectric constant etc. were used to detect the presence of hydrogen bond. Recently, IR[56] and Raman Spectroscopic techniques achieved major importance, though X-rays studies provided the first important structural evidence of the existence and extent of hydrogen bonding. It must be mentioned that till Pauling[54] suggested that the bond is electrostatic in nature no clear idea as regards the nature of the bond was known.

Sidgwick and Bayliss[57] were the first to study the parachor of what they called co-ordinated hydrogen. They found that there is considerable fall in the observed parachors of the compounds like o-nitrophenol, o-hydroxy benzaldehyde, o-vanilin, and carboxylic acids as compared to calculated values for their open chain structures. This fall is enhanced if calculations are made on the basis of closed ring structure by an amount equal to the parachor of the ring formed. The value on the first basis was about–8 units and – 14 units if a ring of six is assumed. It was unfortunate that they did not realise that this drop in parachor was not due to co-ordinate hydrogen but was due to hydrogen bond. Co-ordinated bond at the most can cause a fall of parachor of –1·6 units as shown by Sugden.[1] The co-ordination compounds with normal co-ordination number do not show this decrease in parachor. We[58] extended this work to several compounds. In addition, solution method of Hammick and Andrews[9] was used, so that substances which were not liquids or could not easily be melted, could also be studied. It was observed that compounds suspected to contain hydrogen bonds, showed uniformaly an appreciable decrease in parachor. We thus suggested that this decrease was due to Hydrogen bonding and thus parachor method like other classical methods could be employed for finding out the existence of hydrogen-bond. The fall due to hydrogen bonding which ranges from 6 to 18 units is so large that it cannot be missed even if their is a slight error in measurement.

The important significance of our work consists in drawing an analogy between the appreciable decrease in parachor of salts in aqueous solutions and the fall in case of hydrogen bond. Since the combination in salts is electro-static in nature, the decrease in parachor is attributed to it and we conclude therefore that hydrogen bond is also electrostatic in nature, as its presence results in appreciable fall in parachor. This supports the modern view of Pauling[54]. All other classical methods show a change in property when hydrogen bond is present but cannot draw any inference about the electrostatic nature of the hydrogen bond.

The discussion on the decrease in parachor due to resonance, hydrogen bonding and ionisation suggests that the parachor observations could at least qualitatively be employed for differentiating these three aspects.

Carboxylic acids[55] are known to exist as dimers in benzene, chloroform and carbon tetrachloride and as monomers in ether. Further, the structures may be represented by resonance[59] or hydrogen bond[60].



[ 8 ]

$$R - C \overset{O \cdots H O}{\underset{O H \cdots O}{}} C - R \qquad \text{(Hydrogen bond)}$$
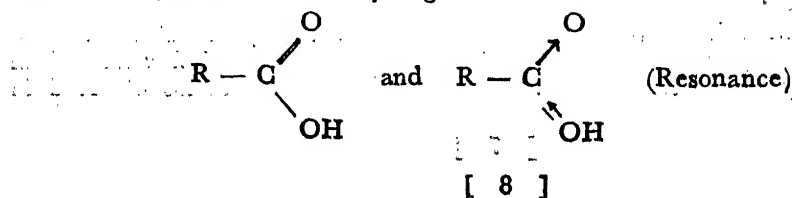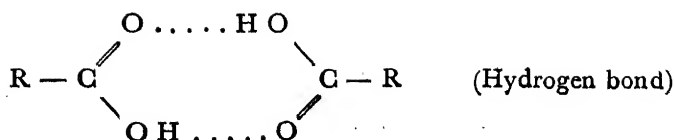
The calculated values of parachor as dimer without hydrogen bond for acetic acid, propionic acid, and benzoic acid are 282, 362 and 550 respectively. The observed results[58] in ether are 284, 362 and 549 while they are 260, 340 and 537 in dimeric solvents. It is concluded, that carboxylic acids mentioned above have resonance structure in ether and hydrogen bonding structure in other solvents as expected.

For amides Pauling[61] has suggested the following resonance structure.

$$R - C \overset{O}{\underset{NH_2}{}} \qquad \text{and} \qquad R - C \overset{C}{\underset{NH_2}{}}$$
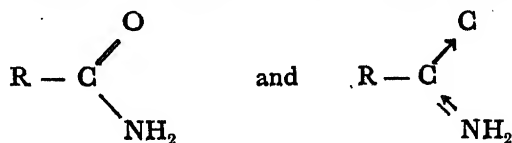
They may form a hydrogen bond[62] as suggested in the case of urea. Wheland suggested their ionisation in aqueous solutions. Our observed results[58] of parachor in methyl alcohol for acetamide benzamide and urea are 148, 279 and 141, respectively, while the calculated values are 151, 279 and 142. The value for acetamide falls appreciably in aqueous solutions. It is clear therefore that the parachor rules out hydrogen bonding in amides and explains the lowering in aqueous solution due to ionisation. Thus it confirms the resonance structures, suggested by Pauling[61], in non-aqueous state and explains why the value should fall in aqueous solutions.

Acetyl acetone[52,63] and acetoacetic ester may have resonance or hydrogen bond structures.
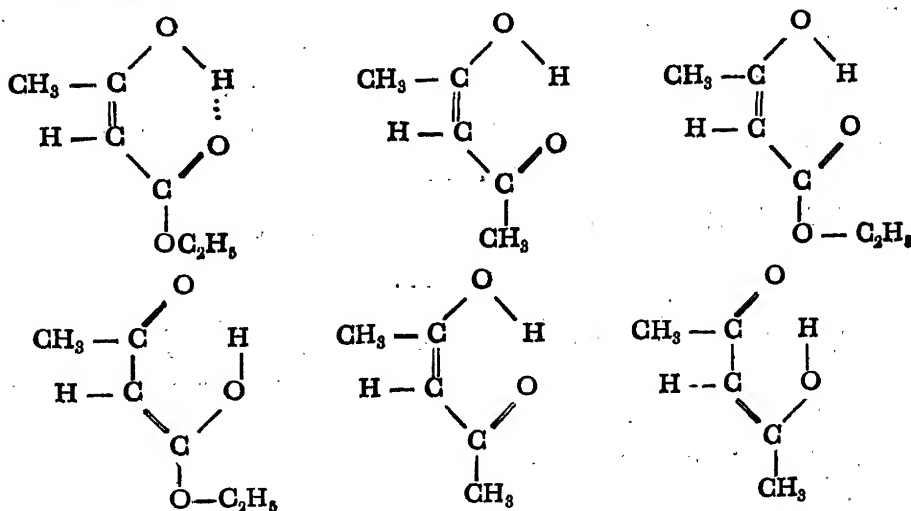
Our[58] parachor value and that of Landolt and Bornstein[64] is 302 for ethyl acetoacetate. The calculated value of 306 is not very different. The results therefore support the resonance structure. The work of Sidgwick[65] on solubility supports

this view. The results with acetyl acetone also support the resonance view as there is hardly a parachor decrease (observed[58],[66] value 245·5 ; calculated 247). However, Pauling[67] has suggested that the bond may be a co-ordinate (not hydrogen bond) one. According to him a second co-ordinate bond for hydrogen is possible. When the bond becomes largley ionic causing appreciable attraction of L electrons, then under this circumstance the proton could use its S orbital for co-ordinate bond formation.

The parachor decrease has clearly established that hydrogen bond is electrostatic in nature and that the values of decrease could suitably be employed to distinguish between resonance, hydrogen bonding and ionisation.

*Hydrogen Bond Energy from Parachor.*

Hydrogen bond may be (*i*) intermolecular, as in case of orthonitro phenol, or (*ii*) intramolecular as in case of alcohols and carboxylic acids. The intramolecular hydrogen bonding in case of carboxylic acids which form dimers, forms a ring, while in alcohols, there is a long chain. The parachor of intermolecular compounds was shown by Büehler[68], Gardner and Clements not to change with temperature, while the parachor of intramolecular compounds with hydrogen bond was found to change due to change in the degree of association with temperature. The carboxylic acids are known to form simplest associated moleeule by forming a dimer and hence are easy for investigating the change in the degree of association with temperature, and therefore for the determination of hydrogen bond energy.

The heats of dissociation of polymers held together by hydrogen bonds have been obtained from the data on change in equalibrium constants with temperature determined by measurement of vapour density or of distribution rates. Thus, the heat of dissociation of gaseous formic acid was found by Coolidge[69] to be 14,125 cals per gram mol.

In case of gaseous acetic acid Fenton and Garner[70] got a value 14900, while Mac Dougall[71] obtained a value of 16400 cals, per gm mol. Hendrixon's[72], values by partition coefficient method in benzene and water and in chloroform and water are 8710 cal and 8350 cals for benzoic acid and 5630 cals and 7680 cals, per gm. mol for salicylic acid. We[73] consider the case of acetic acid which exists at any temperature as an equilibrium mixture of simple molecules and dimer molecules with hydrogen bond.

$$2\ CH_3\ COOH \rightleftarrows CH_3 - C \genfrac{}{}{0pt}{}{O\ \ldots\ H-O}{O-H\ \ldots\ O} C - CH_3$$
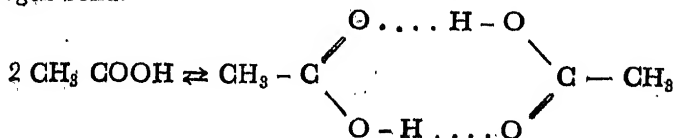
The values for parachor at different temperatures for acetic acid are give by Sudgen[74]. Employing their values the equilibrium constants for the above equilibrium at different temperatures were calculated. Then using the well known expression $\dfrac{d\,lnk}{dT} = \dfrac{Q}{RT^2}$

Q, the energy of hydrogen bond, could be found. Following table illustrates the results.

| Temp. °C | 10 | 50 | 130 | 190 | 250 | 280 |
|---|---|---|---|---|---|---|
| K | 0·044 | 0·311 | 2·51 | 8·14 | 23·83 | 51·03 |
| Q | — | 8923 | 8945 | 7249 | 8598 | 14580 cals. |

The value obtained by Fenton and Garner[70] is 14900 cals. It will be seen therefore that parachor variation with temperature gives an idea that the energy of hydrogen bonds of the same order as found by other methods.

In my address I have discussed briefly the use of parachor in various fields of importance. There are several problems which still need clarification, such as the parachor of ions, the relation of parachor decrease to the strength of the bond. Pimental and A. Meclellan in their book on 'The hydrogen bond' say 'Shukla and Bhagwat' make the pertinent point that a fixed group parachor value for H bonding cannot be expected because various H bonds are different and give different lowering. As yet no extensive systematic study has been reported." It is left therefore to those of the younger generation to try in this direction if it thinks that parachor property though simple can lead to useful results.

Let me once again thank the Council of National Academy of Sciences for having given me the honour of presiding over the Physical Sciences Section of this learned Academy.

### References

1. Sugden, *J. Chem. Soc.*, 1061, (1929).
2. Sugden, and Wilkins, *ibid*, (1292, 1929).
3. Jaeger, *Z. f. anorgan Chem.*, **101**, 1, (1917).
4. Born, *Z. Physik*, **1**, 45, (1920).
5. Mumford and Phillips, *J. Chem. Soc.*, 2130, (1929).
6. Pauling, *J. Amer. Chem. Soc.*, **49**, 765, (1927).
7. Lakhani, and Daroga, *J. Indian Chem. Soc.*, **15**, 37, (1938).
8. Ray. *ibid.*, **15**, 43, (1938).
9. Hammick and Andrews, *J. Chem. Soc.*, 754, (1929).
10. Bhagwat and Toshniwal, *J. Indian Chem. Soc.*, **19**, 225, (1942).
11. Bhagwat and Khandeker, *ibid*, 29, 37, 301, (1952).
12. Toshniwal Ph.D. Thesis, Agra University (1945); Bhagwat, R. P. Shukla, and Gupta, *J. Indian Chem. Soc.*, **26**, 39, (1949); **29**, 701, (1952).
13. Langmuir. *J. Amer. Chem. Soc.*, **41**, 1592, (1919).
14. Copley. *Chem. and Ind.*, **59**, 675, (1940).
15. Sugden. Parachor and Valency, 186, (1930).
16. Kaweeshwar and Vaidya, *Z. Physik. Chem.*, **211**, 108, (1959).
17. Jones and Ray, *J. Amer. Chem. Soc.*, **63**, 3262, (1941).
18. Sun and Silverman, *J. Phys. Chem.*, **47**, 50, (1943).
19. Lee, *J. Chienese Chem. Soc.*, **9**, 46, (1942).
20. Triche, *Bull. Soc.*, **11**, 149, (1944).
21. Liska. *Chem. Zvesti*, **16**, 784 (1962); *Sb. Prac. Chem. Fak. Sust*, **25**, (1962).
22. Pauling, *J. Chem. Physics.*, **1**, 362, 606, 679, (1933).
23. Pauling. Nature of Chemical Bond, 130, (1948).
24. Glasstone. Recent Advances in Physical Chemistry, 91, (1938).
25. Pauling. Nature of Chemical Bond, 194, (1948).
26. Glasstone. Recent Advances in Physical Chemistry, 176–177, (1938).
27. Bhagwat and R. P. Shukla, *J. Indian, Chem. Soc.*, **27**, 283, (1950); **28**, 106, (1951); *Agra, Univ. J. Res.* **2**, II 159 173, 187, (1953).
28. Pauling. Nature of Chemical Bond, 207, (1948).
29. Sugden, *J. Chem. Soc.*, 1177, (1924).
30. Hunter and Maass, *J. Amer. Chem. Soc.*, **51**, 153, (1930).
31. Sugden. Parachor and Valency, 40, (1929).
32. W. Hückel. Theoretical principles of Organic Chemistry Vol. II. 311, (1958).

33. Bhagwat and Kaweeshwar, *Agra Univ. J. Res.*, **3**, Part 1, 181, (1954); *J. Indian Chem . Soc.*, **30**, 571, (1929).
34. Mumford and Phillips, *J. Chem. Soc.*, 75, (1950).
35. Edger and Calingaert, *J. Amer. Chem. Soc.*, **51**, 1540, (1929).
36. Richards, Speyers and Carver, *J. Chem. Soc.*, 1196, (1924).
37. Vogel, *J. Chem. Soc.*, 33, 1758, (1934); 1336, (1938); 1862, (1939); 171, 1528, (1940); 16, 637, (1943); 133, (1946); 607, 1804, (1948).
38. Gibling, *J. Chem. Soc.*, 229, (1941); 661, (1942); 146, (1943); 380, (1944); 236, (1945).
39. Quayle and Donaldson, *J. Amer. Chem. Soc.*, **43**, 72, 35, (1950).
40. Harkins, Clark and Roberts, *J. Amer. Chem. Soc.*, **43**, 35, (1921).
41. Pauling. Nature of Chemical Bond, 196, (1948).
42. Quinn, *J. Amer. Chem. Soc.*, **49**, 2710, (1927).
43. Sugden, Reed and Wilkins, *J. Chem Soc.*, 1525, (1925).
44. Pauling, Nature of Chemical Bond, 197, (1948).
45. Pauling, Nature of Chemical Bond, 135, (1948).
46. Pauling, Nature of Chemical Bond, 195, (1948).
47. W. Nernst, *Z. Physik, Chem.*, **8**, 110, (1891).
48. A. Werner. *Ber.*, **36**, 147, (1903).
49. Moor and Winmill, *J. Chem. Soc.*, **101**, 1635, (1912).
50. Latimer and Rodebush, *J. Amer. Chem. Soc.*, **42**, 1419, (1920).
51. Lowery, *J. Chem. Soc.*, 822, (1923).
52. Lowery, and H. Burgess, *J. Chem. Soc.*, 2111, (1923).
53. Sidgwick, *J. Chem. Soc.*, 527, 2672, (1924).
54. Pauling, *J. Amer. Chem. Soc.*, **57**, 2680, (1938).
55. Lassettre. *Chem. Revs.*, **20**, 259–303, (1937); *J. Amer. Chem. Soc.*, 59, 1383, (1937).
56. Hunter, *Chem. Soc. Ann. Reports*, **43**, 141, (1946); Davies, M. *Ann. Repts. on Progress Chem.*, **43**, 5–30, 1946.
57. Sidgwick, and Bayliss, *J. Chem. Soc.*, 2027, (1930).
58. Bhagwat, and Co-workers, *J. Indian Chem Soc.*, **29**, 679, (1952); **30**, 574, (1953); *Agra Univ. J. Res.*, 2(II), 202, (1953): 3(I), 1, (1954); **4**(I), 1, (1955); 5(II), 357, (1956); 6(I), 39, (1957); 6(I), 55, (1957).
59. Pauling, Nature of Chemical Bond, 202, (1948).
60. Pauling, Nature of Chemical Bond, 306, (1948).
61. Pauling, Nature of Chemical Bond, 207, (1948).
62. Pauling, Nature of Chemical Bond, 315, (1948).
63. Glasstone, Recent Advances in Physical Chemistry, 94, (1938).
64. Landolt and Bornstein. *Zwit. Erganzungsband*, 184, (1931).
65. Sidgwick, *J. Chem. Soc.*, 909, 2739, (1925).
66. Sudgen, *J. Chem. Soc.*, 316, (1929).
67. Pauling, Nature of Chemical Bond, 318, (1948).
68. Buehler, Gardner and Clements, *J. Org. Chem.*, **2**, 172, (1938).
69. Coolidge, *J. Amer. Chem. Soc.*, **50**, 2166, (1928).
70. Fenton and Garner, *J. Chem. Soc.*, **132**, 694, (1930).
71. Mac Dougall, *J. Amer. Chem. Soc.*, **53**, 2585, (1936).
72. Hendrixon, *Z. Anorg. Allegen Chem.*, **13**, 73, (1897).
73. Bhagwat, and Shastry, *Vikram Univ. J. Res.*, **7**, 1, (1963).
74. Sugden, Parachor and Valency, 167, (1930).

# THE

# National Academy of Sciences, India

## THIRTY-NINTH ANNUAL SESSION

ROORKEE, March, 6, 7, and 8, 1970

## GENERAL PRESIDENTIAL ADDRESS

### Oxidation of Simple Organic Compounds

*By*

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# PRESIDENTIAL ADDRESS

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LADIES AND GENTLEMEN.

I am thankful to the members of the National Academy of Sciences for the honour they have bestowed on me by electing me their President for the year 1969.

For many years now I have been interested in the oxidation of simple organic compounds because the complicated food materials that we eat are first broken into simple molecules and then they are oxidised. Moreover, the oxidation of organic molecules is a phenomenon of great importance to the organic and bio-chemists as many of their products are the result of oxidation of organic molecules.

At present, although an electro-chemist is able to compare the oxidising powers of various inorganic reagents by reference to a scale of oxidation—reduction potentials, this approach is of little value to the organic chemist as the majority of the oxidation reactions are not thermodynamically reversible systems. Whereas reversible oxidation—reduction inorganic systems contain mobile electrons, which can be exchanged at the electrodes, the electrons of organic compounds are, in general firmly bound by covalent linkages ; hence a considerable amount of energy is needed for their removal. In order to interpret the organic oxidation reactions theoretically, a general study regarding their quatitative and kinetic aspects is of prime improtance.

The study of the reaction rates is of great importance in industry also. The economic success of a chemical process must depends to a great extent on the intimate knowledge of the conditions of concentrations, temperature, nature of catalyst etc. that influence the reaction rates.

The newer concept of reaction mechanism is of considerable importance here. This includes a knowledge of each individual step that takes place simultaneously or consecutively to produce the observed over all reaction. It is also very necessary to have a detailed stereo-chemical picture of each step. This was emphasised in 1955[1]. This means that one should have some idea of the composition and the geometry of the activated complex.

Further, in order to get a complete picture of oxidation of any organic molecule, the thermodynamic parameters of the process and the products of the reaction should be carefully studied ; often the effect of environment, such as

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1. Chtterji, A. C. Presidential address of the Silver Jubilee Session of the National Academy of Sciences, India, 27-12-1955 page 2.

changes in the acidity brought about by adding various acids, the nature of the solvent, whether organic or inorganic, has considerable influence on the rate and even mechanism of the reaction.

Oxidation of labelled molecules and presence of bases stronger than $H_2O$ gives valuable indication as regards the course of the reaction.

Another important method will be to make a systematic study of the oxidation of simple organic molecules by different oxidising agents to find out their relative oxidising powers as well as to know if different products are produced indicating differ nt paths of reaction mechanism.

In this laboratory oxidation of saturated alcohols, aldehydes and a-glycols by chromic acid in acid medium has been undertaken. Primary, secondary and tertiary alcohols have been oxidised. With a-glycols effect of methyl substitution has been studied.

The order of the reaction with respect to the organic molecules mentioned above has been found to be one. It is also one with respect to chromic acid. It has been established that all the oxidation reactions studied here are bi-molecular acid catalysed reactions. The order with respect to $H^+$ is one at low concentration and two at high concentration of the acid[1].

In the case of oxidation of ethylene glycols and its substitution products, it has been found that the order of the reaction with respect to the alcohol, chromic acid and hydrog n is one, one and two for all $H^+$ ion concentration but with pinacol the order is one, one and one at all hydrogen ion concentration[2].

As the general trend of the order of the reaction with respect to various reactants appears to be the same or nearly the same, an oxidation mechanism of a very similar or nearly similar nature has been proposed.

It is of great interest from the general chemical point of view; (i) to find out if the oxidation involves the transfer of an oxygen atom from the oxidant molecule to the organic molecule undergoing oxidation, or if the oxidation process is a case of dihydrogenation, only (ii) then which of the hydrogen atom is attacked. H of the C-H bond or H of the O-H bond (iii) to know if it is an electron transfer only, (iv) to measure the amount of energy required in affecting the cleavage of C-C bond, (v) to identify the nature of C-C bond rupture and to see whether it is of heterolytic or homolytic kind and lastly; (vi) to find out if the reaction takes place in one electron step or two electron step.
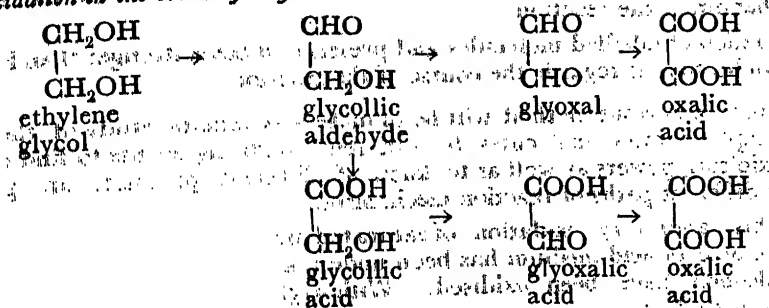
A critical examination of the attempts to elucidate the mechanism of organic molecules by chromic acid shows that a general correlation cannot easily be made although a similar trend may be observed in all. Many substances are smoothly and completely oxidis d but special postulates have often been found necessary in order to explain the idiosyncrasies of individual compounds of the same class.

In the study of the oxidation of glycols care should be taken to identify the products of the reaction as these may oxidise in the ordinary way or there may be a cleavage of the C-C bonds as indicated below :
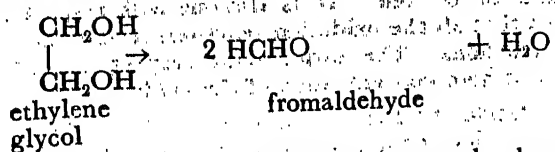
1. Anatony and Chatterji. *Proc. Nat. Academy of Sci. Allahabad India,* 23A, 20, 1954 ; *Zeit Anorg. allg Chemie* 280, 110, 1955, *Z. phys. Chemie* 210, 50, 1959 *ibid,* 210, 103, 1959.

2. Chatterji and Mukherji. *Zeit Phys. Chem.* 208, 281, 1958, *Ibid,* 210, 166, 1959, *ibid.* 210, 255, 1959.

(1) *Oxidation in the ordinary way.*

$$CH_2OH \atop CH_2OH$$ ethylene glycol $\rightarrow$ $$CHO \atop CH_2OH$$ glycollic aldehyde $\rightarrow$ $$CHO \atop CHO$$ glyoxal $\rightarrow$ $$COOH \atop COOH$$ oxalic acid

$$COOH \atop CH_2OH$$ glycollic acid $\rightarrow$ $$COOH \atop CHO$$ glyoxalic acid $\rightarrow$ $$COOH \atop COOH$$ oxalic acid

(2) *Oxidation with the rupture of the C–C bond*

$$CH_2OH \atop CH_2OH$$ ethylene glycol $\rightarrow$ $2\ HCHO$ fromaldehyde $+\ H_2O$

Sometimes both the types of oxidation occur and glyoxal and formaldihyde are produced simultaneously.

From the large amount of data obtained by us during our investigation it is of interest to compare the variation of thermodynamical parameters of the oxidation of monohydric alcohols with α–glycols when their hydrogen is substituted by methyl group progressively. The results obtained in the case of methyl, ethyl, isopropyl and butyl alcohols along with the ones of ethylene, propylene, 2·3 butylene glycols and penacol are given here.

*Oxidation of methyl, ethyl, isopropyl and ter-butyl alcohols by chromic acid, relative entropies heats and free energies of activation\**

| | Chromic Acid = 0·0020 M | | Perchloric Acid = 0·3055 M | | | | | |
|---|---|---|---|---|---|---|---|---|
| Alcohol | $k\,35°$ sec$^{-1}$ | $k\,45°$ sec$^{-1}$ | Temp. coeff. | $E$ $k$ cals | $A$ sec$^{-1}$ | $\Delta S^{\neq} - \Delta S_0^{\neq}$ Cal/°C | $\Delta H^{\neq} - \Delta H_0^{\neq}$ Cal | $\Delta G^{\neq} - \Delta G_0^{\neq}$ Cal |
| Methyl Alcohol (0·5 M) | $4·00 \times 10^{-5}$ | $7·33 \times 10^{-5}$ | 1·83 | 13·2 | $9·25 \times 10^4$ | 0 | 0 | 0 |
| Ethyl Alcohol (0·5 M) | $9·35 \times 10^{-4}$ | $1·77 \times 10^{-3}$ | 1·89 | 11·6 | $1·59 \times 10^5$ | 8·3 | 600 | −1900 |
| Isopropyl Alcohol (0·5 M) | $9·77 \times 10^{-4}$ | $1·97 \times 10^{-3}$ | 2·02 | 13·7 | $9·16 \times 10^6$ | 12·4 | 1800 | −2000 |
| Ter-Butyl Alcohol (0·5 M) | $7·72 \times 10^{-7}$ | $1·68 \times 10^{-6}$ | 2·18 | 13·2 | $1·78 \times 10^3$ | −3·5 | 3000 | 2400 |

*\*unpublished.*

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| **Chromic Acid = 0·002 M** | | | | **Perchloric Acid = 0·2175 M** | | | | |
| Glycol | $k 25°$ sec$^{-1}$ | $k 35°$ sec$^{-1}$ | Temp. Coeff. | E $k$ cals | A sec$^{-1}$ | $\Delta S^{\neq} - \Delta S_0^{\neq}$ cal/°C | $\Delta H^{\neq} - \Delta H_0^{\neq}$ cal | $\Delta G^{\neq} - \Delta G_0^{\neq}$ cal |
| Ethylene glycol (0·02 M) | $2·98 \times 10^{-6}$ | $5·36 \times 10^{-6}$ | 1·80 | 10·7 | $2·09 \times 10^{2}$ | 0 | 0 | 0 |
| Propylene glycol (0 02 M) | $1·81 \times 10^{-5}$ | $3·20 \times 10^{-5}$ | 1·77 | 10·4 | $7·63 \times 10^{2}$ | 2·6 | −300 | −1100 |
| 2 : 3 Butylene glycol (0·02 M) | $4·82 \times 10^{-5}$ | $9·38 \times 10^{-5}$ | 1·95 | 12·2 | $4·25 \times 10^{4}$ | 10·4 | 1400 | −1700 |
| Pinacol (0·02 M) | $1·14 \times 10^{-3}$ | $2·93 \times 10^{-3}$ | 2·57 | 17·2 | $4·64 \times 10^{9}$ | 33·8 | 6500 | −3700 |

*Chatterji, A. C. and Mukherji, S. M., *Zeit. Fur Physik. Chemie*, 210 166 175, 1959.

On critically examining the tables of both the sets we find the rate increasing upto isopropylalcohol and 2·3 butylene glycol respectively so that the rate increases so long as there is a hydrogen atom attached to the carbon atom next to the one carrying the OH. But when it comes to the butyl alcohol and pinacol where all the carbon atoms have been replaced, the behaviour is different. With butyl alcohol the rate is considerably decreased while in pinacol the rate is very much increased. The difference in the behaviour of the two tertiary alcohols point to the difference in the mechanism. Chromic acid converts pinacol to acetone quite rapidly. It must necessarily involve the attack on O-H bond. This is not sufficient reason for the increase in the rate. Here the oxidation proceeds via the oxygen diradtical Me₂ - C - C Me₂ whereas in butyl alcohol no free radical is produced.

$$Me_2 - \underset{\underset{O^*}{|}}{C} - \underset{\underset{O^*}{|}}{C} Me_2 \quad \text{produced.}$$

When we examine the products formed by the rupture of C - C bond *i.e.* formaldehyde, acetaldehyde ard acetone in ethylene glycol, butylene glycol and pinacol we find the yields to be 1·2%, 28·7%, 67%. Thus we see that the rupture increases as H is replaced by methyl group.

It has also been found that ethylene glycol yields more glyoxal than formaldehyde. This is always not so, with different oxidisers different oxidation products are produced in different quantities even with ethylene glycol. Anodic oxidation gives 91% of glycollic aldehyde[2]. With aryl iodoso acetate, chromyl chloride, lead tetraacetate and periodic acid almost, quantitative rupture takes

1. Chatterji and Mukherji. *Zeit Physik. Chemie*, 210, 172, 1959.
2. Glasstone and Hickling. *J. Chem. Soc.*, 820, 1936.

plcce and formaldehyde is obtained in almost quantitative yield, whilst $KMnO_4$ in acid media gives large quantity of glyoxal. Hence, we see that the same organic molecule is sometimes ruptured quantitatively by some oxidisers whilst other oxidisers produce almost very little rupture products.

It is also very peculiar that with the same oxidising agent $(HCrO_4)^-$ the main seat of reaction is shifted as we go up the homologous series of glycols. There is absolutely no doubt that the O–H bond (bond energy 110·2 K cals/mole) is much stronger in an isolated molecule than the C–H bond (bond energy is 87·3 K cals/mole) but this may not be true under all circumstances. Pauling[1] thinks that the O–H bond has about 40% ionic character and this electrostatic distribution to the bond strength may be so low in a medium of high dielectric constant (*e.g.* water, acetic acid, ethyl alcohol etc.) as to make the O–H bond more suseptible to attack than the C–H bond.

Accoding to Coulson ("Valence" Oxford Clarendon Press) 1952 page 301, the bond energies of O–H . . . O, and C–H . . . O are 5·9 ± 0·2 and 2·6 K cals/mole respectively. It seems, therefore, that there is a tendency of the chromic acid molecule to form an ester.

By comparing the activation energies of the glycols we find that the value is much higher in pinacol that in ethylene glycol or 2·3 butylene glycol. In the cases where methyl group has replaced the hydrogen, the formation of cyclic complexes is increased by the increase in the availability of electron on the oxygen atom of the O–H bond    Here the increase in reactivity with the substitution of methyl group for hydrogen may be attributed to an entropy effect    The variation in the energy of activation is relatively unimportant in this case.

The free energy of activation represents the reactivity of a molecule. The more reactive one will have lower free energy of activation. The data shows a very good parallelism with the oxidation rates.

As a result of works carried out by R. Criegee in Germany ; Westheimer in America, Jan Rocek in Czechoslovakia and later on in America and Chatterji in India the following points have arisen.

(1) The reaction is acid catalysed, the rate is one or two with respect to $H^+$ ion conc ; but the rate is always unity with respect to the oxidiser and the alcohol.

(2) The reaction is much faster in acetic acid than in mineral acids of the same $H_0$ concentration.

(3) The transition state consists of a mono-chromium and not a di-chromium species.

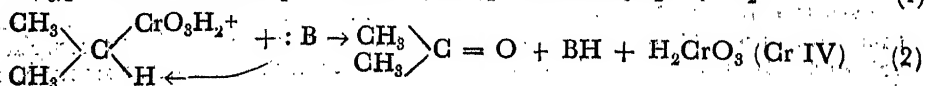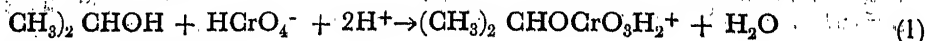(4) There is a kinetic isotope effect of 6·6 at 25°C for the oxidation of $(CH_3)_2$ CDOH.

(5) Addition of magnous ion reduces the rate of reduction by a factor of 2.

(6) Esters of chromic radical has been isolated both with monohydric alcohols as well as glycols.
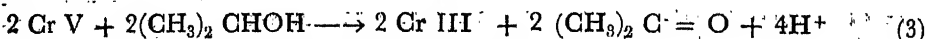
In order to explain all the above facts ester mechanism is the most probable path of the reaction.

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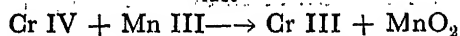1. Laiders book on Chemical kinetics, p. 135, 1950.

[ 5 ]

After ester has been formed, its decomposition takes place by the removal of proton to any available base with the elemination of Cr (IV) (equation 2).

$$CH_3)_2 \, CHOH + HCrO_4^- + 2H^+ \rightarrow (CH_3)_2 \, CHOCrO_3H_2^+ + H_2O \tag{1}$$

$$\begin{array}{c}CH_3 \\ \diagdown \\ CH_3\end{array} C \begin{array}{c}CrO_3H_2^+ \\ \diagup \quad \diagdown \\ H \leftarrow\end{array} + : B \rightarrow \begin{array}{c}CH_3 \\ \diagdown \\ CH_3\end{array} C = O + BH + H_2CrO_3 \, (Cr \, IV) \tag{2}$$

followed by Cr IV + Cr VI → 2 Cr (V)

$$2 \, Cr \, V + 2(CH_3)_2 \, CHOH \longrightarrow 2 \, Cr \, III + 2 \, (CH_3)_2 \, C = O + 4H^+ \tag{3}$$

or by Cr IV + Mn II $\xrightarrow{}$ Cr III + Mn III

$$Cr \, IV + Mn \, III \xrightarrow{fast} Cr \, III + MnO_2$$

This suggests that in the case of ethylene to butylene glycols, the rate determining step involves the rupture of C – H bond. It has been assumed that the same mechanism as in the case of isopropyl alcohol operates in the case of these glycols also.

In the case of pinacol and also with other glycols, the mechanism of glycol decomposition may be represented as follows :
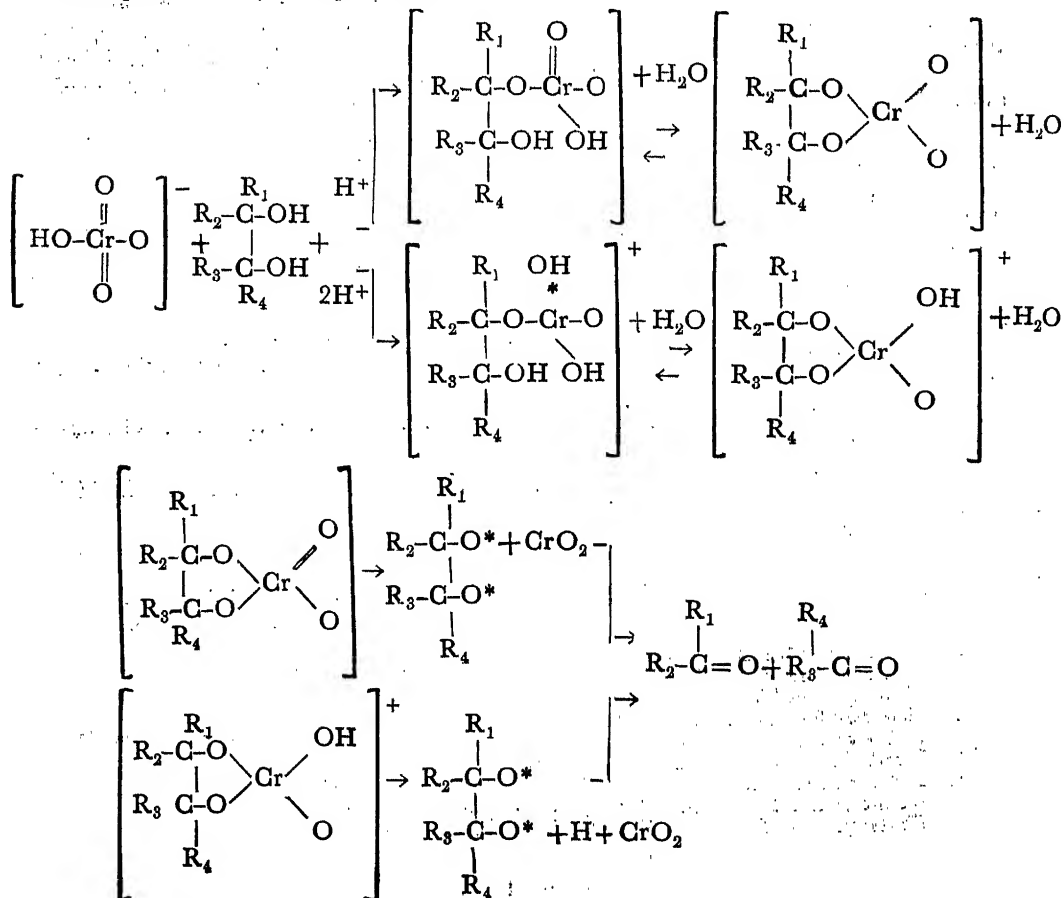
The main point of the above mechanism is the removal of H by a base. In the case of aqueous solution water molecules have been assumed to act as a base. The participation of the base in the decomposition of the ester has proved difficult although Lee and Westheimer[1] prepared the ester of isopropyl alcohol and showed that its decomposition in benzene is accelerated by prydine. This suggests that ester mechanism is a most reasonable assumption but this assumption has not been substantiated as it has not been proved that ester is an intermediate in the oxidation under ordinary conditions.

We have isolated the esters of many alcohols that we have studied from the reaction mixture itself. The chromic acid ester of n-propyl, isopropyle, n-butyl, iso-butyl, sec-butyl and n-hexyl alcohols has been isolated in benzene and carbon tetrachloride layers when these were added to the reaction mixtures[2]. Similarly the chromic acid ester of pinacol has been extracted by benzene from the reaction mixture[3].

Other workers have also extracted esters during the oxidation of alcohols such as tricyclohexy-carbinol[4] and tri phenyl carbinol oxidation[5]. Many others have also isolated the ester in the case of ali cylic alcohols. Hence the formation of ester as an intermediate is fairly well established during the oxidation process.

Now about the other assumption that water acts as a base to remove H has been investigated by many workers. Attempts have been made to carry out the oxidation reaction in the presence of bases stronger than $H_2O$. Previously Westheimer and co-workers[6] tried to find out if the addition of pyridine accelerated the rate of reaction. They reported that the reaction is slightly but significantly catalysed.

Roc k and Knupicka[7] disputed this. They measured the rate of oxidation of isopropyl alcohol by adding crystalline pyridium perchlorate to the reaction solution. It is not very clear why Westheimer and Rocek expected that the rate should be increased in their system. They added pyridium perchlorite to the system containing alcohol, chromic acid and perchloric acid. Here pyridium perchlorate primarily dissociates to a large extent and hydrolyses to a very small extent. Hence free pyridine is present in a very small quantity if at all, hence no acceleration should be produced.

We have observed the rate of oxidation of isopropyl and sec. butyl alcohol[8]. We have also observed the oxidation of ethylene alcohol, propylene glycol and pinacol by chromic acid in pyridene-pyridium ion[9] buffer solutions whilst pyridene in this solution accelerates the rate in all case it does not do so in the case of pinacol. Pinacol does not contain any hydrogen which can be removed by the base hence no acceleration should be observed.

This conforms the ester mechanism.

In the end I am thankful to you for kindly giving me a patient hearing.

1. Leo and Westheimer, *J. A. C. S.* **74**, 4383, 1952
2. Chatterji and Mukherji, *Zeit Physik. Chemie*, **228**, 159, 1965.
3. Chatterji and Mukherji, *Zeit Physik. Chemie*, **228**, 116, 1965
4. Neunhoeffer, *Ann* **509**, 115, 1934.
5. Anber et al, *J. Chem. Soc.* 3603, 1954.
6. Westheimer and co-workers, *J. A. C. S.* **73**, 65, 1951.
7. Rocek and Krupicka. *Coll. Czech. Chem. Cooun*, **23**, 2068, 1958.
8. Chatterji and Mukherji. *Zeit Physik Chem.* **228**, 159, 1965.
9. Chatterji and Mukherji. *Zeit Physik Chem.* **228**, 166, 1965.